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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10L 1/18, 1/22	A1	(11) International Publication Number: WO 97/43357 (43) International Publication Date: 20 November 1997 (20.11.97)
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(21) International Application Number: PCT/US97/07941
(22) International Filing Date: 12 May 1997 (12.05.97)

(30) Priority Data:
08/647,486 14 May 1996 (14.05.96) US
08/833,463 7 April 1997 (07.04.97) US

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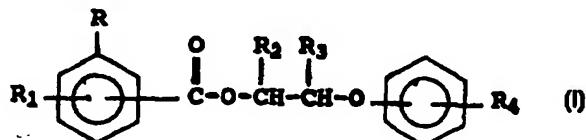
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(81) Designated States: AU, BR, CA, CN, JP, KR, MX, NZ, SG,
European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB,
GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: FUEL ADDITIVE COMPOSITIONS CONTAINING AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS AND POLY(OXYALKYLENE) AMINES



(57) Abstract

A fuel additive composition comprising: (a) an aromatic ester compound of formula (I), or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_n-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and X is O or I; R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and (b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel fuel range. The fuel additive compositions of this invention are useful as fuel additives for the prevention and control of engine deposits.

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FUEL ADDITIVE COMPOSITIONS CONTAINING
AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS
AND POLY(OXYALKYLENE) AMINES

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to fuel additive compositions containing aromatic esters of polyalkylphenoxyalkanols and poly(oxyalkylene) amines. In a further aspect, this invention relates to the use of these additive compositions in fuel compositions to prevent and control engine deposits.

Description of the Related Art

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Krauz et al., discloses a motor fuel

01 composition comprising a mixture of hydrocarbons in the
02 gasoline boiling range containing about 0.01 to 0.25 volume
03 percent of a high molecular weight aliphatic
04 hydrocarbon-substituted phenol in which the aliphatic
05 hydrocarbon radical has an average molecular weight in the
06 range of about 500 to 3,500. This patent teaches that
07 gasoline compositions containing minor amounts of an
08 aliphatic hydrocarbon-substituted phenol not only prevent or
09 inhibit the formation of intake valve and port deposits in a
10 gasoline engine, but also enhance the performance of the
11 fuel composition in engines designed to operate at higher
12 operating temperatures with a minimum of decomposition and
13 deposit formation in the manifold of the engine.

14
15 Similarly, U.S. Patent No. 4,134,846, issued January 16,
16 1979 to Machleder et al., discloses a fuel additive
17 composition comprising a mixture of (1) the reaction product
18 of an aliphatic hydrocarbon-substituted phenol,
19 epichlorohydrin and a primary or secondary mono- or
20 polyamine, and (2) a polyalkylene phenol. This patent
21 teaches that such compositions show excellent carburetor,
22 induction system and combustion chamber detergency and, in
23 addition, provide effective rust inhibition when used in
24 hydrocarbon fuels at low concentrations.

25
26 Amino phenols are also known to function as
27 detergents/dispersants, antioxidants and anti-corrosion
28 agents when used in fuel compositions. U.S. Patent
29 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
30 example, discloses amino phenols having at least one
31 substantially saturated hydrocarbon-based substituent of at
32 least 30 carbon atoms. The amino phenols of this patent are
33 taught to impart useful and desirable properties to
34 oil-based lubricants and normally liquid fuels.

01 Similarly, U.S. Patent No. 3,149,933, issued September 22,
02 1964 to K. Ley et al., discloses hydrocarbon-substituted
03 amino phenols as stabilizers for liquid fuels.

04
05 U.S. Patent No. 4,386,939, issued June 7, 1983 to
06 R. M. Lange, discloses nitrogen-containing compositions
07 prepared by reacting an amino phenol with at least one 3- or
08 4-membered ring heterocyclic compound in which the hetero
09 atom is a single oxygen, sulfur or nitrogen atom, such as
10 ethylene oxide. The nitrogen-containing compositions of
11 this patent are taught to be useful as additives for
12 lubricants and fuels.

13
14 Nitro phenols have also been employed as fuel additives.
15 For example, U.S. Patent No. 4,347,148, issued August 31,
16 1982 to K. E. Davis, discloses nitro phenols containing at
17 least one aliphatic substituent having at least about
18 40 carbon atoms. The nitro phenols of this patent are
19 taught to be useful as detergents, dispersants, antioxidants
20 and demulsifiers for lubricating oil and fuel compositions.

21
22 Similarly, U.S. Patent No. 3,434,814, issued March 25, 1969
23 to M. Dubeck et al., discloses a liquid hydrocarbon fuel
24 composition containing a major quantity of a liquid
25 hydrocarbon of the gasoline boiling range and a minor amount
26 sufficient to reduce exhaust emissions and engine deposits
27 of an aromatic nitro compound having an alkyl, aryl,
28 aralkyl, alkanoyloxy, alkoxy, hydroxy or halogen
29 substituent.

30
31 More recently, certain poly(oxyalkylene) esters have been
32 shown to reduce engine deposits when used in fuel
33 compositions. U.S. Patent No. 5,211,721, issued May 18,
34 1993 to R. L. Sung et al., for example, discloses an oil

01 soluble polyether additive comprising the reaction product
02 of a polyether polyol with an acid represented by the
03 formula RCOOH in which R is a hydrocarbyl radical having
04 6 to 27 carbon atoms. The poly(oxyalkylene) ester compounds
05 of this patent are taught to be useful for inhibiting
06 carbonaceous deposit formation, motor fuel hazing, and as
07 ORI inhibitors when employed as soluble additives in motor
08 fuel compositions.

09
10 Poly(oxyalkylene) esters of amino- and nitrobenzoic acids
11 are also known in the art. For example, U.S. Patent
12 No. 2,714,607, issued August 2, 1955 to M. Matter, discloses
13 polyethoxy esters of aminobenzoic acids, nitrobenzoic acids
14 and other isocyclic acids. These polyethoxy esters are
15 taught to have excellent pharmacological properties and to
16 be useful as anesthetics, spasmolytics, analeptics and
17 bacteriostatics.

18
19 Similarly, U.S. Patent No. 5,090,914, issued February 25,
20 1992 to D. T. Reardan et al., discloses poly(oxyalkylene)
21 aromatic compounds having an amino or hydrazinocarbonyl
22 substituent on the aromatic moiety and an ester, amide,
23 carbamate, urea or ether linking group between the aromatic
24 moiety and the poly(oxyalkylene) moiety. These compounds
25 are taught to be useful for modifying macromolecular species
26 such as proteins and enzymes.

27
28 U.S. Patent No. 4,328,322, issued September 22, 1980 to
29 R. C. Baron, discloses amino- and nitrobenzoate esters of
30 oligomeric polyols, such as poly(ethylene) glycol. These
31 materials are used in the production of synthetic polymers
32 by reaction with a polyisocyanate.

33
34

01 U.S. Patent No. 4,859,210, issued August 22, 1989 to
02 Franz et al., discloses fuel compositions containing (1) one
03 or more polybutyl or polyisobutyl alcohols wherein the
04 polybutyl or polyisobutyl group has a number average
05 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)
06 of the polybutyl or polyisobutyl alcohol, or (3) a
07 carboxylate ester of the polybutyl or polyisobutyl alcohol.
08 This patent further teaches that when the fuel composition
09 contains an ester of a polybutyl or polyisobutyl alcohol,
10 the ester-forming acid group may be derived from saturated
11 or unsaturated, aliphatic or aromatic, acyclic or cyclic
12 mono- or polycarboxylic acids.

13
14 U.S. Patent Nos. 3,285,855, and 3,330,859 issued
15 November 15, 1966 and July 11, 1967 respectively, to
16 Dexter et al., disclose alkyl esters of dialkyl
17 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the
18 ester moiety contains from 6 to 30 carbon atoms. These
19 patents teach that such esters are useful for stabilizing
20 polypropylene and other organic material normally subject to
21 oxidative deterioration. Similar alkyl esters containing
22 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.
23 Patent No. 5,196,565, which issued March 23, 1993 to Ross.

24
25 U.S. Patent No. 5,196,142, issued March 23, 1993 to
26 Mollet et al., discloses alkyl esters of hydroxyphenyl
27 carboxylic acids wherein the ester moiety may contain up to
28 23 carbon atoms. This patent teaches that such compounds
29 are useful as antioxidants for stabilizing
30 emulsion-polymerized polymers.

31
32 Commonly assigned U.S. Patent No. 5,407,452, issued
33 April 18, 1995, and corresponding International Application
34 Publication No. WO 95/04118, published February 9, 1995,

01 disclose certain poly(oxyalkylene) nitro and aminoaromatic
02 esters having from 5 to 100 oxyalkylene units and teach the
03 use of such compounds as fuel additives for the prevention
04 and control of engine deposits.

05
06 Similarly, commonly assigned U.S. Patent No. 5,427,591,
07 issued June 27, 1995, and corresponding International
08 Application Publication No. WO 94/14926, published July 7,
09 1994, disclose certain poly(oxyalkylene) hydroxyaromatic
10 esters which are useful as fuel additives to control engine
11 deposits.

12
13 In addition, commonly assigned U.S. Patent No. 5,380,345,
14 issued January 10, 1995, and corresponding International
15 Application Publication No. WO 95/15366, published June 8,
16 1995, disclose certain polyalkyl nitro and aminoaromatic
17 esters useful as deposit control additives for fuels.
18 Moreover, commonly assigned International Application
19 Publication No. WO 95/11955, published May 4, 1995,
20 discloses certain polyalkyl hydroxyaromatic esters which are
21 also useful as deposit control fuel additives.

22
23 Poly(oxyalkylene) amines are also well known in the art as
24 fuel additives for the prevention and control of engine
25 deposits. For example, U.S. Patent No. 4,191,537, issued
26 March 4, 1980 to R. A. Lewis et al., discloses a fuel
27 composition comprising a major portion of hydrocarbons
28 boiling in the gasoline range and from 30 to 2000 ppm of a
29 hydrocarbyl poly(oxyalkylene) aminocarbamate having a
30 molecular weight from about 600 to 10,000, and at least one
31 basic nitrogen atom. The hydrocarbyl poly(oxyalkylene)
32 moiety is composed of oxyalkylene units selected from 2 to

33
34

01 5 carbon oxyalkylene units. These fuel compositions are
02 taught to maintain the cleanliness of intake systems without
03 contributing to combustion chamber deposits.

04

05 U.S. Patent No. 5,112,364, issued May 12, 1992 to
06 Rath et al., discloses gasoline-engine fuels which contain
07 small amounts of a polyetheramine and/or a polyetheramine
08 derivative, wherein the polyetheramine is prepared by
09 reductive amination of a phenol-initiated or alkylphenol-
10 initiated polyether alcohol with ammonia or a primary amine.

11

12 U.S. Patent No. 4,247,301, issued January 27, 1981 to
13 Honnen, discloses hydrocarbyl-substituted poly(oxyalkylene)
14 polyamines, wherein the hydrocarbyl group contains from 1 to
15 30 carbon atoms and the polyamine moiety contains from 2 to
16 12 amine nitrogen atoms and from 2 to 40 carbon atoms. This
17 patent teaches that the additives may be prepared by the
18 reaction of a suitable hydrocarbyl-terminated polyether
19 alcohol with a halogenating agent, such as HCl or thionyl
20 chloride, to form a polyether chloride, followed by reaction
21 of the polyether chloride with a polyamine to form the
22 desired poly(oxyalkylene) polyamine. This patent also
23 teaches at Example 6 that the polyether chloride may be
24 reacted with ammonia or dimethylamine to form the
25 corresponding polyether amine or polyether dimethylamine.

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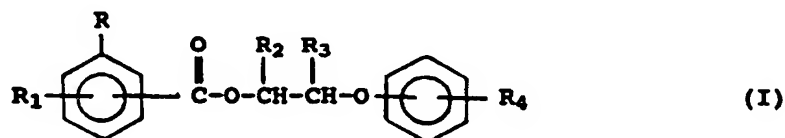
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SUMMARY OF THE INVENTION

It has now been discovered that the combination of certain aromatic esters of polyalkylphenoxyalkanols with poly(oxyalkylene) amines affords a unique fuel additive composition which provides excellent control of engine deposits, especially intake valve and combustion chamber deposits.

Accordingly, the present invention provides a novel fuel additive composition comprising:

- (a) an aromatic ester compound having the following formula or a fuel soluble salt thereof:



wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and

01 (b) a poly(oxyalkylene) amine having at least one basic
02 nitrogen atom and a sufficient number of oxyalkylene
03 units to render the poly(oxyalkylene) amine soluble in
04 hydrocarbons boiling in the gasoline or diesel fuel
05 range.

06

07 The present invention further provides a fuel composition
08 comprising a major amount of hydrocarbons boiling in the
09 gasoline or diesel range and an effective
10 deposit-controlling amount of a compound of the present
11 invention.

12

13 The present invention additionally provides a fuel
14 concentrate comprising an inert stable oleophilic organic
15 solvent boiling in the range of from about 150°F. to 400°F.
16 and from about 10 to 70 weight percent of a compound of the
17 present invention.

18

19 Among other factors, the present invention is based on the
20 surprising discovery that the unique combination of certain
21 aromatic esters of polyalkylphenoxyalkanols with
22 poly(oxyalkylene) amines provides excellent control of
23 engine deposits, especially on intake valves and in
24 combustion chambers, when employed as additives in fuel
25 compositions.

26

27 DETAILED DESCRIPTION OF THE INVENTION

28

29 The Aromatic Ester of Polyalkylphenoxyalkanols

30

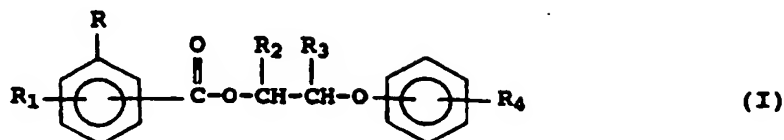
31 The aromatic ester component of the present additive
32 composition is an aromatic ester of a

33

34

-10-

01 polyalkylphenoxyalkanol and has the following general
02 formula:



08 or a fuel-soluble salt thereof, wherein R, R₁, R₂, R₃ and R₄
09 are as defined hereinabove.

10

11 Based on performance (e.g. deposit control), handling
12 properties and performance/cost effectiveness, the preferred
13 aromatics ester compounds employed in the present invention
14 are those wherein R is nitro, amino, N-alkylamino, or
15 —CH₂NH₂ (aminomethyl). More preferably, R is a nitro,
16 amino or —CH₂NH₂ group. Most preferably, R is an amino or
17 —CH₂NH₂ group, especially amino. Preferably, R₁ is
18 hydrogen, hydroxy, nitro or amino. More preferably, R₁ is
19 hydrogen or hydroxy. Most preferably, R₁ is hydrogen.
20 Preferably, R₄ is a polyalkyl group having an average
21 molecular weight in the range of about 500 to 3,000, more
22 preferably about 700 to 3,000, and most preferably about 900
23 to 2,500. Preferably, the compound has a combination
24 of preferred substituents.

25

26 Preferably, one of R₂ and R₃ is hydrogen or lower alkyl of 1
27 to 4 carbon atoms, and the other is hydrogen. More
28 preferably, one of R₂ and R₃ is hydrogen, methyl or ethyl,
29 and the other is hydrogen. Most preferably, R₂ is hydrogen,
30 methyl or ethyl, and R₃ is hydrogen.

31

32 When R and/or R₁ is an N-alkylamino group, the alkyl group
33 of the N-alkylamino moiety preferably contains 1 to 4 carbon
34

01 atoms. More preferably, the *N*-alkylamino is *N*-methylamino
02 or *N*-ethylamino.

03

04 Similarly, when *R* and/or *R*₁ is an *N,N*-dialkylamino group,
05 each alkyl group of the *N,N*-dialkylamino moiety preferably
06 contains 1 to 4 carbon atoms. More preferably, each alkyl
07 group is either methyl or ethyl. For example, particularly
08 preferred *N,N*-dialkylamino groups are *N,N*-dimethylamino,
09 *N*-ethyl-*N*-methylamino and *N,N*-diethylamino groups.

10

11 A further preferred group of compounds are those wherein *R*
12 is amino, nitro, or -CH₂NH₂ and *R*₁ is hydrogen or hydroxy.

13 A particularly preferred group of compounds are those
14 wherein *R* is amino, *R*₁, *R*₂ and *R*₃ are hydrogen, and *R*₄ is a
15 polyalkyl group derived from polyisobutene.

16

17 It is preferred that the *R* substituent is located at the
18 meta or, more preferably, the para position of the benzoic
19 acid moiety, i.e., para or meta relative to the carbonyloxy
20 group. When *R*₁ is a substituent other than hydrogen, it is
21 particularly preferred that this *R*₁ group be in a meta or
22 para position relative to the carbonyloxy group and in an
23 ortho position relative to the *R* substituent. Further, in
24 general, when *R*₁ is other than hydrogen, it is preferred
25 that one of *R* or *R*₁ is located para to the carbonyloxy group
26 and the other is located meta to the carbonyloxy group.
27 Similarly, it is preferred that the *R*₄ substituent on the
28 other phenyl ring is located para or meta, more preferably
29 para, relative to the ether linking group.

30

31 The compounds employed in the present invention will
32 generally have a sufficient molecular weight so as to be
33 non-volatile at normal engine intake valve operating
34 temperatures (about 200°-250°C). Typically, the molecular

-12-

01 weight of the compounds employed in this invention will
02 range from about 700 to about 3,500, preferably from about
03 700 to about 2,500.

04

05 Fuel-soluble salts of the compounds of formula I can be
06 readily prepared for those compounds containing an amino or
07 substituted amino group and such salts are contemplated to
08 be useful for preventing or controlling engine deposits.
09 Suitable salts include, for example, those obtained by
10 protonating the amino moiety with a strong organic acid,
11 such as an alkyl- or arylsulfonic acid. Preferred salts are
12 derived from toluenesulfonic acid and methanesulfonic acid.

13

14 When the R or R₁ substituent is a hydroxy group, suitable
15 salts can be obtained by deprotonation of the hydroxy group
16 with a base. Such salts include salts of alkali metals,
17 alkaline earth metals, ammonium and substituted ammonium
18 salts. Preferred salts of hydroxy-substituted compounds
19 include alkali metal, alkaline earth metal and substituted
20 ammonium salts.

21

22 Definitions

23

24 As used herein, the following terms have the following
25 meanings unless expressly stated to the contrary.

26

27 The term "amino" refers to the group: -NH₂.

28

29 The term "N-alkylamino" refers to the group: -NHR_a wherein
30 R_a is an alkyl group. The term "N,N-dialkylamino" refers to
31 the group: -NR_bR_c, wherein R_b and R_c are alkyl groups.

32

33 The term "alkyl" refers to both straight- and branched-chain
34 alkyl groups.

01 The term "lower alkyl" refers to alkyl groups having 1 to
02 about 6 carbon atoms and includes primary, secondary and
03 tertiary alkyl groups. Typical lower alkyl groups include,
04 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
05 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

06

07 The term "polyalkyl" refers to an alkyl group which is
08 generally derived from polyolefins which are polymers or
09 copolymers of mono-olefins, particularly 1-mono-olefins,
10 such as ethylene, propylene, butylene, and the like.
11 Preferably, the mono-olefin employed will have 2 to about
12 24 carbon atoms, and more preferably, about 3 to 12 carbon
13 atoms. More preferred mono-olefins include propylene,
14 butylene, particularly isobutylene, 1-octene and 1-decene.
15 Polyolefins prepared from such mono-olefins include
16 polypropylene, polybutene, especially polyisobutene, and the
17 polyalphaolefins produced from 1-octene and 1-decene.

18

19 The term "fuel" or "hydrocarbon fuel" refers to normally
20 liquid hydrocarbons having boiling points in the range of
21 gasoline and diesel fuels.

22

23 General Synthetic Procedures

24

25 The polyalkylphenoxyalkyl aromatic esters employed in this
26 invention may be prepared by the following general methods
27 and procedures. It should be appreciated that where typical
28 or preferred process conditions (e.g., reaction
29 temperatures, times, mole ratios of reactants, solvents,
30 pressures, etc.) are given, other process conditions may
31 also be used unless otherwise stated. Optimum reaction
32 conditions may vary with the particular reactants or
33 solvents used, but such conditions can be determined by one
34 skilled in the art by routine optimization procedures.

01 Those skilled in the art will also recognize that it may be
02 necessary to block or protect certain functional groups
03 while conducting the following synthetic procedures. In
04 such cases, the protecting group will serve to protect the
05 functional group from undesired reactions or to block its
06 undesired reaction with other functional groups or with the
07 reagents used to carry out the desired chemical
08 transformations. The proper choice of a protecting group
09 for a particular functional group will be readily apparent
10 to one skilled in the art. Various protecting groups and
11 their introduction and removal are described, for example,
12 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
13 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,
14 and references cited therein.

15
16 In the present synthetic procedures, a hydroxyl group will
17 preferably be protected, when necessary, as the benzyl or
18 tert-butyldimethylsilyl ether. Introduction and removal of
19 these protecting groups is well described in the art. Amino
20 groups may also require protection and this may be
21 accomplished by employing a standard amino protecting group,
22 such as a benzyloxycarbonyl or a trifluoroacetyl group.
23 Additionally, as will be discussed in further detail
24 hereinbelow, the aromatic esters employed in this invention
25 having an amino group on the aromatic moiety will generally
26 be prepared from the corresponding nitro derivative.
27 accordingly, in many of the following procedures, a nitro
28 group will serve as a protecting group for the amino moiety.

29
30 Moreover, the aromatic ester compounds employed in this
31 invention having a $-CH_2NH_2$ group on the aromatic moiety will
32 generally be prepared from the corresponding cyano
33 derivative, $-CN$. Thus, in many of the following procedures,

34

01 a cyano group will serve as a protecting group for the
02 $-\text{CH}_2\text{NH}_2$ moiety.

03

04 Synthesis

05

06 The polyalkylphenoxyalkyl aromatic esters employed in the
07 present invention may be prepared by a process which
08 initially involves hydroxyalkylation of a polyalkylphenol of
09 the formula:

10

11

12



(II)

13

14

15 wherein R_4 is as defined herein, with an alkylene carbonate
16 of the formula:

17

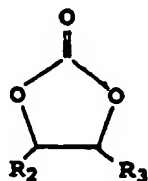
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22



(III)

23

24 wherein R_2 and R_3 are as defined herein, in the presence of
25 a catalytic amount of an alkali metal hydride or hydroxide,
26 or alkali metal salt, to provide a polyalkylphenoxyalkanol
27 of the formula:

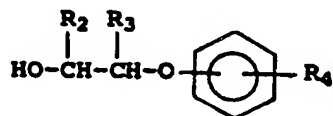
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(IV)

33 wherein R_2 , R_3 and R_4 are as defined herein.

34

01 The polyalkylphenols of formula II are well known materials
02 and are typically prepared by the alkylation of phenol with
03 the desired polyolefin or chlorinated polyolefin. A further
04 discussion of polyalkylphenols can be found, for example, in
05 U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

06
07 Accordingly, the polyalkylphenols of formula II may be
08 prepared from the corresponding olefins by conventional
09 procedures. For example, the polyalkylphenols of formula II
10 above may be prepared by reacting the appropriate olefin or
11 olefin mixture with phenol in the presence of an alkylating
12 catalyst at a temperature of from about 25°C. to 150°C., and
13 preferably 30°C. to 100°C. either neat or in an essentially
14 inert solvent at atmospheric pressure. A preferred
15 alkylating catalyst is boron trifluoride. Molar ratios of
16 reactants may be used. Alternatively, molar excesses of
17 phenol can be employed, i.e., 2 to 3 equivalents of phenol
18 for each equivalent of olefin with unreacted phenol
19 recycled. The latter process maximizes monoalkylphenol.
20 Examples of inert solvents include heptane, benzene,
21 toluene, chlorobenzene and 250 thinner which is a mixture of
22 aromatics, paraffins and naphthenes.

23
24 The polyalkyl substituent on the polyalkylphenols employed
25 in the invention is generally derived from polyolefins which
26 are polymers or copolymers of mono-olefins, particularly
27 1-mono-olefins, such as ethylene, propylene, butylene, and
28 the like. Preferably, the mono-olefin employed will have 2
29 to about 24 carbon atoms, and more preferably, about 3 to
30 12 carbon atoms. More preferred mono-olefins include
31 propylene, butylene, particularly isobutylene, 1-octene and
32 1-decene. Polyolefins prepared from such mono-olefins
33 include polypropylene, polybutene, especially polyisobutene,
34

01 and the polyalphaolefins produced from 1-octene and
02 1-decene.

03

04 The preferred polyisobutenes used to prepare the presently
05 employed polyalkylphenols are polyisobutenes which comprise
06 at least about 20% of the more reactive methylvinylidene
07 isomer, preferably at least 50% and more preferably at least
08 70%. Suitable polyisobutenes include those prepared using
09 BF_3 catalysts. The preparation of such polyisobutenes in
10 which the methylvinylidene isomer comprises a high
11 percentage of the total composition is described in U.S.
12 Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes,
13 known as "reactive" polyisobutenes, yield high molecular
14 weight alcohols in which the hydroxyl group is at or near
15 the end of the hydrocarbon chain. Examples of suitable
16 polyisobutenes having a high alkylvinylidene content include
17 Ultravis 30, a polyisobutene having a number average
18 molecular weight of about 1300 and a methylvinylidene
19 content of about 74%, and Ultravis 10, a polyisobutene
20 having a number average molecular weight of about 950 and a
21 methylvinylidene content of about 76%, both available from
22 British Petroleum.

23

24 The alkylene carbonates of formula III are known compounds
25 which are available commercially or can be readily prepared
26 using conventional procedures. Suitable alkylene carbonates
27 include ethylene carbonate, propylene carbonate,
28 1,2-butylene carbonate, 2,3-butylene carbonate, and the
29 like. A preferred alkylene carbonate is ethylene carbonate.

30

31 The catalyst employed in the reaction of the polyalkylphenol
32 and alkylene carbonate may be any of the well known
33 hydroxyalkylation catalysts. Typical hydroxyalkylation
34 catalysts include alkali metal hydrides, such as lithium

-18-

01 hydride, sodium hydride and potassium hydride, alkali metal
02 hydroxides, such as sodium hydroxide and potassium
03 hydroxide, and alkali metal salts, for example, alkali metal
04 halides, such as sodium chloride and potassium chloride, and
05 alkali metal carbonates, such as sodium carbonate and
06 potassium carbonate. The amount of catalyst employed will
07 generally range from about 0.01 to 1.0 equivalent,
08 preferably from about 0.05 to 0.3 equivalent.

09
10 The polyalkylphenol and alkylene carbonate are generally
11 reacted in essentially equivalent amounts in the presence of
12 the hydroxyalkylation catalyst at a temperature in the range
13 of about 100°C. to 210°C., and preferably from about 150°C.
14 to about 170°C. The reaction may take place in the presence
15 or absence of an inert solvent.

16
17 The time of reaction will vary depending on the particular
18 alkylphenol and alkylene carbonate reactants, the catalyst
19 used and the reaction temperature. Generally, the reaction
20 time will range from about two hours to about five hours.
21 The progress of the reaction is typically monitored by the
22 evolution of carbon dioxide. At the completion of the
23 reaction, the polyalkylphenoxyalkanol product is isolated
24 using conventional techniques.

25
26 The hydroxyalkylation reaction of phenols with alkylene
27 carbonates is well known in the art and is described, for
28 example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030
29 and 4,341,905.

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01 Alternatively, the polyalkylphenoxyalkanol product of
02 formula IV may be prepared by reacting the polyalkylphenol
03 of formula II with an alkylene oxide of the formula:



09 wherein R₂ and R₃ are as defined herein, in the presence of
10 a hydroxyalkylation catalyst as described above.
11 Suitable alkylene oxides of formula V include ethylene
12 oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene
13 oxide, and the like. A preferred alkylene oxide is ethylene
14 oxide.

15
16 In a manner similar to the reaction with alkylene carbonate,
17 the polyalkylphenol and alkylene oxide are reacted in
18 essentially equivalent or equimolar amounts in the presence
19 of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst,
20 such as sodium or potassium hydride, at a temperature in the
21 range of about 30°C. to about 150°C., for about 2 to about
22 24 hours. The reaction may be conducted in the presence or
23 absence of a substantially anhydrous inert solvent.
24 Suitable solvents include toluene, xylene, and the like.
25 Generally, the reaction conducted at a pressure sufficient
26 to contain the reactants and any solvent present, typically
27 at atmospheric or higher pressure. Upon completion of the
28 reaction, the polyalkylphenoxyalkanol is isolated by
29 conventional procedures.

30
31 The polyalkylphenoxyalkanol of formula IV is subsequently
32 reacted with a substituted benzoic acid of formula VI to
33
34

-20-

01 provide the aromatic ester compounds of formula I. This
 02 reaction can be represented as follows:

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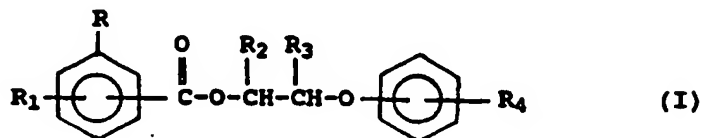
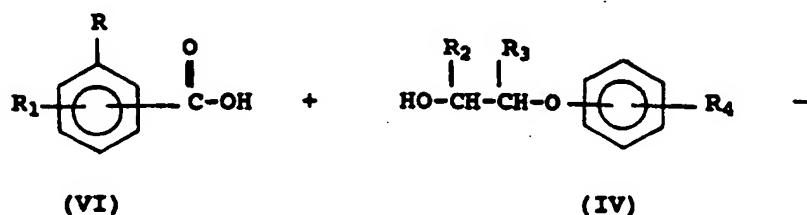
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wherein R, R₁, R₂, R₃ and R₄ are as defined herein, and wherein any hydroxy or amino substituent on the substituted benzoic acid of formula VI is preferably protected with a suitable protecting group, for example, a benzyl or nitro group, respectively. Moreover, a -CH₂NH₂ substituent on the aromatic ring will preferably be protected by the use of a cyano group, CN.

This reaction is typically conducted by contacting a polyalkylphenoxyalkanol of formula IV with about 0.25 to about 1.5 molar equivalents of the corresponding substituted and protected benzoic acid of formula VI in the presence of an acidic catalyst at a temperature in the range of about 70°C. to about 160°C. for about 0.5 to about 48 hours. Suitable acid catalysts for this reaction include p-toluene sulfonic acid, methanesulfonic acid and the like. Optionally, the reaction can be conducted in the presence of an inert solvent, such as benzene, toluene and the like. The water generated by this reaction is preferably removed

01 during the course of the reaction, for example, by
02 azeotropic distillation.

03

04 The substituted benzoic acids of formula VI are generally
05 known compounds and can be prepared from known compounds
06 using conventional procedures or obvious modifications
07 thereof. Representative acids suitable for use as starting
08 materials include, for example, 2-aminobenzoic acid
09 (anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic
10 acid, 3-amino-4-hydroxybenzoic acid,
11 4-amino-3-hydroxybenzoic acid, 2-nitrobenzoic acid,
12 3-nitrobenzoic acid, 4-nitrobenzoic acid,
13 3-hydroxy-4-nitrobenzoic acid, 4-hydroxy-3-nitrobenzoic
14 acid. When the R substituent is $-\text{CH}_2-\text{NR}_5\text{R}_6$, suitable
15 starting materials include 4-cyanobenzoic acid and
16 3-cyanobenzoic acid.

17

18 Preferred substituted benzoic acids include 3-nitrobenzoic
19 acid, 4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid,
20 4-hydroxy-3-nitrobenzoic acid, 3-cyanobenzoic acid and
21 4-cyanobenzoic acid.

22

23 The compounds of formula I or their suitably protected
24 analogs also can be prepared by reacting the
25 polyalkylphenoxyalkanol of formula IV with an acid halide of
26 the substituted benzoic acid of formula VI such as an acid

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01 chloride or acid bromide. This can be represented by the
 02 following reaction equation:

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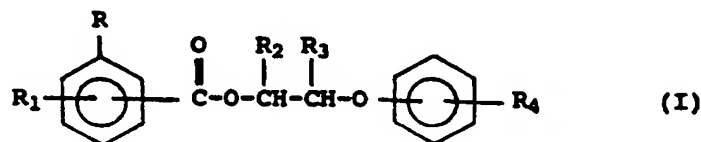
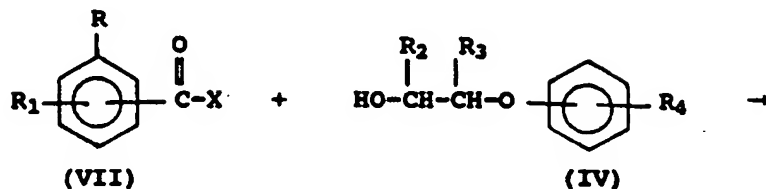
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wherein X is halide, typically chloride or bromide, and R, R₁, R₂, R₃ and R₄ are as defined herein above, and wherein any hydroxy or amino substituents on the acid halide of formula VII are preferably protected with a suitable protection group, for example, benzyl or nitro, respectively. Also, when R is —CH₂NR₅R₆, a suitable starting material is a cyanobenzoyl halide.

Typically, this reaction is conducted by contacting the polyalkylphenoxyalkanol of formula IV with about 0.9 to about 1.5 molar equivalents of the acid halide of formula VII in an inert solvent, such as, for example, toluene, dichloromethane, diethyl ether, and the like, at a temperature in the range of about 25°C. to about 150°C. The reaction is generally complete in about 0.5 to about 48 hours. Preferably, the reaction is conducted in the presence of a sufficient amount of an amine capable of neutralizing the acid generated during the reaction, such

-23-

01 as, for example, triethylamine, di(isopropyl)ethylamine,
02 pyridine or 4-dimethylaminopyridine.

03

04 When the benzoic acids of formula VI or acid halides of
05 formula VII contain a hydroxyl group, protection of the
06 aromatic hydroxyl groups may be accomplished using
07 well-known procedures. The choice of a suitable protecting
08 group for a particular hydroxybenzoic carboxylic acid will
09 be apparent to those skilled in the art. Various protecting
10 groups, and their introduction and removal, are described,
11 for example, in T. W. Greene and P. G. M. Wuts, *Protective*
12 *Groups in Organic Synthesis*, Second Edition, Wiley,
13 New York, 1991, and references cited therein.

14

15 After completion of the esterification, deprotection of the
16 aromatic hydroxyl group can also be accomplished using
17 conventional procedures. Appropriate conditions for this
18 deprotection step will depend upon the protecting group(s)
19 utilized in the synthesis and will be readily apparent to
20 those skilled in the art. For example, benzyl protecting
21 groups may be removed by hydrogenolysis under 1 to about
22 4 atmospheres of hydrogen in the presence of a catalyst,
23 such as palladium on carbon. Typically, this deprotection
24 reaction is conducted in an inert solvent, preferably a
25 mixture of ethyl acetate and acetic acid, at a temperature
26 of from about 0°C. to about 40°C. for about 1 to about
27 24 hours.

28

29 When the benzoic acids of formula VI or acyl halides of
30 formula VII have a free amino group (-NH₂) on the phenyl
31 moiety, it is generally desirable to first prepare the
32 corresponding nitro compound (i.e., where R and/or R₁ is a
33 nitro group) using the above-described synthetic procedures,
34 including preparation of the acyl halides, and then reduce

01 the nitro group to an amino group using conventional
02 procedures. Aromatic nitro groups may be reduced to amino
03 groups using a number of procedures that are well known in
04 the art. For example, aromatic nitro groups may be reduced
05 under catalytic hydrogenation conditions; or by using a
06 reducing metal, such as zinc, tin, iron and the like, in the
07 presence of an acid, such as dilute hydrochloric acid.
08 Generally, reduction of the nitro group by catalytic
09 hydrogenation is preferred. Typically, this reaction is
10 conducted using about 1 to 4 atmospheres of hydrogen and a
11 platinum or palladium catalyst, such as palladium on carbon.
12 The reaction is typically carried out at a temperature of
13 about 0°C. to about 100°C. for about 1 to 24 hours in an
14 inert solvent, such as ethanol, ethyl acetate and the like.
15 Hydrogenation of aromatic nitro groups is discussed in
16 further detail in, for example, P. N. Rylander, *Catalytic*
17 *Hydrogenation in Organic Synthesis*, pp. 113-137, Academic
18 Press (1979); and *Organic Synthesis, Collective Vol. I*,
19 Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941);
20 and references cited therein.

21
22 Likewise, when the benzoic acids of formula VI or acyl
23 halides of formula VII contain a $-\text{CH}_2\text{NH}_2$ group on the phenyl
24 moiety, it is generally desirable to first prepare the
25 corresponding cyano compounds (i.e., where R and/or R_1 is a
26 $-\text{CN}$ group), and then reduce the cyano group to a $-\text{CH}_2\text{NH}_2$
27 group using conventional procedures. Aromatic cyano groups
28 may be reduced to $-\text{CH}_2\text{NH}_2$ groups using procedures well
29 known in the art. For example, aromatic cyano groups may be
30 reduced under catalytic hydrogenation conditions similar to
31 those described above for reduction of aromatic nitro groups
32 to amino groups. Thus, this reaction is typically conducted
33 using about 1 to 4 atmospheres of hydrogen and a platinum or
34

01 palladium catalyst, such as palladium on carbon. Another
02 suitable catalyst is a Lindlar catalyst, which is palladium
03 on calcium carbonate. The hydrogenation may be carried out
04 at temperatures of about 0°C. to about 100°C. for about 1 to
05 24 hours in an inert solvent such as ethanol, ethyl acetate,
06 and the like. Hydrogenation of aromatic cyano groups is
07 further discussed in the references cited above for
08 reduction of aromatic nitro groups.

09
10 The acyl halides of formula VII can be prepared by
11 contacting the corresponding benzoic acid compound of
12 formula VI with an inorganic acid halide, such as thionyl
13 chloride, phosphorous trichloride, phosphorous tribromide,
14 or phosphorous pentachloride; or with oxalyl chloride.
15 Typically, this reaction will be conducted using about 1 to
16 5 molar equivalents of the inorganic acid halide or oxalyl
17 chloride, either neat or in an inert solvent, such as
18 diethyl ether, at a temperature in the range of about 20°C.
19 to about 80°C. for about 1 to about 48 hours. A catalyst,
20 such as *N,N*-dimethylformamide, may also be used in this
21 reaction. Again it is preferred to first protect any
22 hydroxy or amino substituents before converting the benzoic
23 acid to the acyl halide.

24

25 The Poly(oxyalkylene) Amine

26

27 The poly(oxyalkylene) amine component of the present fuel
28 additive composition is a poly(oxyalkylene) amine having at
29 least one basic nitrogen atom and a sufficient number of
30 oxyalkylene units to render the poly(oxyalkylene) amine
31 soluble in hydrocarbons boiling in the gasoline or diesel
32 range.

33

34

01 Preferably, such poly(oxyalkylene) amines will also be of
02 sufficient molecular weight so as to be nonvolatile at
03 normal engine intake valve operating temperatures, which are
04 generally in the range of about 200°C to 250°C.

05
06 Generally, the poly(oxyalkylene) amines suitable for use in
07 the present invention will contain at least about
08 5 oxyalkylene units, preferably about 5 to 100, more
09 preferably about 8 to 100, and even more preferably about 10
10 to 100. Especially preferred poly(oxyalkylene) amines will
11 contain about 10 to 25 oxyalkylene units.

12
13 The molecular weight of the presently employed
14 poly(oxyalkylene) amines will generally range from about 500
15 to about 10,000, preferably from about 500 to about 5,000.

16
17 Suitable poly(oxyalkylene) amine compounds for use in the
18 present invention include hydrocarbyl poly(oxyalkylene)
19 polyamines as disclosed, for example, in U.S. Patent
20 No. 4,247,301, issued January 27, 1981 to Honnen, the
21 disclosure of which is incorporated herein by reference.
22 These compounds are hydrocarbyl poly(oxyalkylene) polyamines
23 wherein the poly(oxyalkylene) moiety comprises at least one
24 hydrocarbyl-terminated poly(oxyalkylene) chain of 2 to
25 5 carbon atom oxyalkylene units, and wherein the
26 poly(oxyalkylene) chain is bonded through a terminal carbon
27 atom to a nitrogen atom of a polyamine having from 2 to
28 about 12 amine nitrogen atoms and from 2 to about 40 carbon
29 atoms with a carbon-to-nitrogen ratio between about 1:1 and
30 10:1. The hydrocarbyl group on these hydrocarbyl
31 poly(oxyalkylene) polyamines will contain from about 1 to
32 30 carbon atoms. These compounds generally have molecular
33 weights in the range of about 500 to 10,000, preferably from
34

01 about 500 to 5,000 and more preferably from about 800 to
02 5,000.

03
04 The above-described hydrocarbyl poly(oxyalkylene) polyamines
05 are prepared by conventional procedures known in the art, as
06 taught, for example, in U.S. Patent No. 4,247,301.

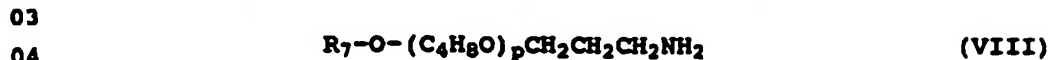
07
08 Other poly(oxyalkylene) amines suitable for use in the
09 present invention are the poly(oxyalkylene) polyamines
10 wherein the poly(oxyalkylene) moiety is connected to the
11 polyamine moiety through an oxyalkylene hydroxy-type linkage
12 derived from an epihalohydrin, such as epichlorohydrin or
13 epibromohydrin. This type of poly(oxyalkylene) amine having
14 an epihalohydrin-derived linkage is described, for example,
15 in U.S. Patent No. 4,261,704, issued April 14, 1981 to
16 Langdon, the disclosure of which is incorporated herein by
17 reference.

18
19 Useful polyamines for preparing the epihalohydrin-derived
20 poly(oxyalkylene) polyamines include, for example, alkylene
21 polyamines, polyalkylene polyamines, cyclic amines, such as
22 piperazines, and amino-substituted amines. The
23 poly(oxyalkylene) polyamines having an epihalohydrin-derived
24 linkage between the poly(oxyalkylene) and polyamine moieties
25 are prepared using known procedures as taught, for example,
26 in U.S. Patent No. 4,261,704.

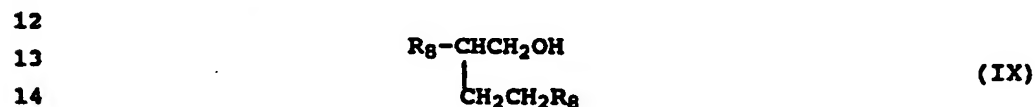
27
28 Another type of poly(oxyalkylene) amine useful in the
29 present invention is a highly branched alkyl
30 poly(oxyalkylene) monoamine as described, for example in
31 U.S. Patent No. 5,094,667, issued March 10, 1992 to
32 Schilowitz et al., the disclosure of which is incorporated
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34

-28-

01 herein by reference. These highly branched alkyl
02 poly(oxyalkylene) monoamines have the general formula:



05 wherein R_7 is a highly branched alkyl group containing from
06 12 to 40 carbon atoms, preferably an alkyl group having
07 20 carbon atoms which is derived from a Guerbet condensation
08 reaction, and p is a number up to 30, preferably 4 to 8.
09 The preferred alkyl group is derived from a Guerbet alcohol
10 containing 20 carbon atoms having the formula:
11



16 wherein R_8 is a hydrocarbyl chain.

17
18 The above highly branched alkyl poly(oxyalkylene) monoamines
19 are prepared by using known methods as disclosed, for
20 example, in U.S. Patent No. 5,094,667.

21
22 A preferred class of poly(oxyalkylene) amine for use in the
23 fuel additive composition of the present invention are
24 hydrocarbyl poly(oxyalkylene) monoamines as described, for
25 example, in U.S. Patent No. 5,112,364, issued May 12, 1992
26 to Rath et al., the disclosure of which is incorporated
27 herein by reference. As disclosed in U.S. Patent
28 No. 5,112,364, such poly(oxyalkylene) monoamines may be
29 prepared by the reductive amination of a phenol-initiated or
30 alkylphenol-initiated poly(oxyalkylene) alcohol with ammonia
31 or a primary amine.

32
33 In addition, the above-mentioned U.S. Patent No. 4,247,301
34 to Honnen discloses hydrocarbyl poly(oxyalkylene) monoamines

01 which are suitable for use in the present fuel additive
02 composition. In particular, Example 6 of this patent
03 describes alkylphenyl poly(oxyalkylene) monoamines prepared
04 from ammonia and dimethylamine.

05

06 A particularly preferred type of hydrocarbyl
07 poly(oxyalkylene) monoamine is an alkylphenyl
08 poly(oxyalkylene) monoamine wherein the poly(oxyalkylene)
09 moiety contains oxypropylene units or oxybutylene units or
10 mixtures of oxypropylene and oxybutylene units. Preferably,
11 the alkyl group on the alkylphenyl moiety is a straight or
12 branched-chain alkyl of 1 to 24 carbon atoms. An especially
13 preferred alkylphenyl moiety is tetrapropenylphenyl, that
14 is, where the alkyl group is a branched-chain alkyl of
15 12 carbon atoms derived from propylene tetramer.

16

17 A further discussion of the hydrocarbon-substituted
18 poly(oxyalkylene) moiety on the poly(oxyalkylene) amine
19 component of the present fuel additive composition is found
20 hereinbelow.

21

22 Another preferred class of poly(oxyalkylene) amine for use
23 in the fuel additive composition of the present invention
24 are hydrocarbyl-substituted poly(oxyalkylene)
25 aminocarbamates disclosed, for example, in U.S. Patent
26 Nos. 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930;
27 4,233,168; 4,197,409; 4,243,798 and 4,881,945, the
28 disclosure of each of which are incorporated herein by
29 reference.

30

31 These hydrocarbyl poly(oxyalkylene) aminocarbamates contain
32 at least one basic nitrogen atom and have an average
33 molecular weight of about 500 to 10,000, preferably about
34 500 to 5,000, and more preferably about 1,000 to 3,000. As

-30-

01 described more fully hereinbelow, these hydrocarbyl
02 poly(oxyalkylene) aminocarbamates contain (a) a
03 poly(oxyalkylene) moiety, (b) an amine moiety and (c) a
04 carbamate connecting group.

05

06 A. The Poly(oxyalkylene) Moiety

07

08 The hydrocarbyl-terminated poly(oxyalkylene) polymers which
09 are utilized in preparing the hydrocarbyl poly(oxyalkylene)
10 aminocarbamates employed in the present invention are
11 monohydroxy compounds, e.g., alcohols, often termed
12 monohydroxy polyethers, or polyalkylene glycol monocarbyl
13 ethers, or "capped" poly(oxyalkylene) glycols, and are to be
14 distinguished from the poly(oxyalkylene) glycols (diols), or
15 polyols, which are not hydrocarbyl-terminated, i.e., are not
16 capped. These hydrocarbyl poly(oxyalkylene) alcohols may be
17 produced by the addition of lower alkylene oxides, such as
18 ethylene oxide, propylene oxide, butylene oxide, etc. to a
19 hydroxy compound, R_9OH , under polymerization conditions,
20 wherein R_9 is the hydrocarbyl group which caps the
21 poly(oxyalkylene) chain.

22

23 In the hydrocarbyl poly(oxyalkylene) aminocarbamates
24 employed in the present invention, the hydrocarbyl group R_9
25 will generally contain from 1 to about 30 carbon atoms,
26 preferably from 2 to about 20 carbon atoms and is preferably
27 aliphatic or aromatic, i.e., an alkyl or alkyl phenyl
28 wherein the alkyl is a straight or branched-chain of from
29 1 to about 24 carbon atoms. More preferably, R_9 is
30 alkylphenyl wherein the alkyl group is a branched-chain of
31 12 carbon atoms, derived from propylene tetramer, and
32 commonly referred to as tetrapropenyl.

33

34

01 The oxyalkylene units in the poly(oxyalkylene) moiety
02 preferably contain from 2 to about 5 carbon atoms but one or
03 more units of a larger carbon number may also be present.
04 Generally, each poly(oxyalkylene) polymer contains at least
05 about 5 oxyalkylene units, preferably about 5 to about
06 100 oxyalkylene units, more preferably about 8 to about
07 100 units, even more preferably about 10 to 100 units, and
08 most preferably 10 to about 25 such units. The
09 poly(oxyalkylene) moiety of the hydrocarbyl
10 poly(oxyalkylene) aminocarbamates employed in the present
11 invention is more fully described and exemplified in U.S.
12 Patent No. 4,191,537, issued March 4, 1980 to Lewis, the
13 disclosure of which is incorporated herein by reference.
14
15 Although the hydrocarbyl group on the hydrocarbyl
16 poly(oxyalkylene) moiety will preferably contain from 1 to
17 about 30 carbon atoms, longer hydrocarbyl groups,
18 particularly longer chain alkyl phenyl groups, may also be
19 employed. For example, alkylphenyl poly(oxyalkylene)
20 aminocarbamates wherein the alkyl group contains at least
21 40 carbon atoms, as described in U.S. Patent No. 4,881,945,
22 issued November 21, 1989 to Buckley, are also contemplated
23 for use in the present invention. The alkyl phenyl group on
24 the aminocarbamates of U.S. Patent No. 4,881,945 will
25 preferably contain an alkyl group of 50 to 200 carbon atoms,
26 and more preferably, an alkyl group of 60 to 100 carbon
27 atoms. These longer chain alkyl groups will generally be
28 derived from olefin polymers, such as polybutene. The
29 disclosure of U.S. Patent No. 4,881,945 is incorporated
30 herein by reference.
31
32 Also contemplated for use in the present invention are
33 alkylphenyl poly(oxypropylene) aminocarbamates wherein the
34 alkyl group is a substantially straight-chain alkyl group.

-32-

01 of about 25 to 50 carbon atoms derived from an alpha olefin
02 oligomer of C₈ to C₂₀ alpha olefins, as described in
03 PCT International Patent Application Publication
04 No. WO 90/07564, published July 12, 1990, the disclosure of
05 which is incorporated herein by reference.

06

07 B. The Amine Moiety

08

09 The amine moiety of the hydrocarbyl poly(oxyalkylene)
10 aminocarbamate is preferably derived from a polyamine having
11 from 2 to about 12 amine nitrogen atoms and from 2 to about
12 40 carbon atoms.

13

14 The polyamine is preferably reacted with a hydrocarbyl
15 poly(oxyalkylene) chloroformate to produce the hydrocarbyl
16 poly(oxyalkylene) aminocarbamate fuel additive finding use
17 within the scope of the present invention. The
18 chloroformate is itself derived from the hydrocarbyl
19 poly(oxyalkylene) alcohol by reaction with phosgene.

20

21 The polyamine provides the hydrocarbyl poly(oxyalkylene)
22 aminocarbamate with, on the average, at least about one
23 basic nitrogen atom per carbamate molecule, i.e., a nitrogen
24 atom titratable by strong acid. The polyamine preferably
25 has a carbon-to-nitrogen ratio of from about 1:1 to about
26 10:1. The polyamine may be substituted with substituents
27 selected from hydrogen, hydrocarbyl groups of from 1 to
28 about 10 carbon atoms, acyl groups of from 2 to about
29 10 carbon atoms, and monoketone, monohydroxy, mononitro,
30 monocyano, alkyl and alkoxy derivatives of hydrocarbyl
31 groups of from 1 to 10 carbon atoms. It is preferred that
32 at least one of the basic nitrogen atoms of the polyamine is
33 a primary or secondary amino nitrogen. The amine moiety of
34 the hydrocarbyl poly(oxyalkylene) aminocarbamates employed

-33-

01 in the present invention has been described and exemplified
02 more fully in U.S. Patent No. 4,191,537.

03

04 A more preferred polyamine for use in preparing the
05 hydrocarbyl poly(oxyalkylene) aminocarbamates finding use
06 within the scope of the present invention is a polyalkylene
07 polyamine, including alkylenediamine, and including
08 substituted polyamines, e.g., alkyl and hydroxyalkyl-
09 substituted polyalkylene polyamine. Preferably, the
10 alkylene group contains from 2 to 6 carbon atoms, there
11 being preferably from 2 to 3 carbon atoms between the
12 nitrogen atoms. Examples of such polyamines include
13 ethylenediamine, diethylenetriamine, triethylenetetramine,
14 di(trimethylene)triamine, dipropylenetriamine,
15 tetraethylenepentamine, etc.

16

17 Among the polyalkylene polyamines, polyethylene polyamine
18 and polypropylene polyamine containing 2 to about 12 amine
19 nitrogen atoms and 2 to about 24 carbon atoms are especially
20 preferred and in particular, the lower polyalkylene
21 polyamines, e.g., ethylenediamine, diethylenetriamine,
22 propylenediamine, dipropylenetriamine, etc., are most
23 preferred.

24

25 C. The Aminocarbamate Connecting Group

26

27 The hydrocarbyl poly(oxyalkylene) aminocarbamate employed as
28 the poly(oxyalkylene) amine component of the fuel additive
29 composition of the present invention is obtained by linking
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01 the polyamine and the hydrocarbyl poly(oxyalkylene) alcohol
02 together through a carbamate linkage, i.e.,

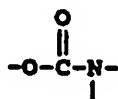
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wherein the oxygen may be regarded as the terminal hydroxyl oxygen of the poly(oxyalkylene) alcohol, the nitrogen is derived from the polyamine and the carbonyl group $-\text{C}(\text{O})-$, is preferably provided by a coupling agent, such as phosgene.

In a preferred method of preparation, the hydrocarbyl poly(oxyalkylene) alcohol is reacted with phosgene to produce a chloroformate and the chloroformate is reacted with the polyamine. Since there may be more than one nitrogen atom of the polyamine which is capable of reacting with the chloroformate, the carbamate product may contain more than one hydrocarbyl poly(oxyalkylene) moiety. It is preferred that the hydrocarbyl poly(oxyalkylene) aminocarbamate product contains on the average, about one poly(oxyalkylene) moiety per molecule (i.e., is a monocarbamate), although it is understood that this reaction route may lead to mixtures containing appreciable amounts of di- or higher poly(oxyalkylene) chain substitution on a polyamine containing several reactive nitrogen atoms.

A particularly preferred aminocarbamate is alkylphenyl poly(oxybutylene) aminocarbamate, wherein the amine moiety is derived from ethylene diamine or diethylene triamine. Synthetic methods to avoid higher degrees of substitution, methods of preparation, and other characteristics of the aminocarbamates used in the present invention are more fully described and exemplified in U.S. Patent No. 4,191,537.

Fuel Compositions

01
02
03 The fuel additive composition of the present invention will
04 generally be employed in hydrocarbon fuels to prevent and
05 control engine deposits, particularly intake valve
06 deposits. The proper concentration of additive necessary to
07 achieve the desired deposit control varies depending upon
08 the type of fuel employed, the type of engine, and the
09 presence of other fuel additives.
10
11 Generally, the present fuel additive composition will be
12 employed in a hydrocarbon fuel in a concentration ranging
13 from about 50 to about 5,000 parts per million (ppm) by
14 weight, preferably from 100 to 2,500 ppm.
15
16 In terms of individual components, hydrocarbon fuel
17 containing the fuel additive composition of this invention
18 will generally contain about 25 to 2,000 ppm of the
19 polyalkylphenoxyalkyl aromatic ester component and about 25
20 to 2,000 ppm of the poly(oxyalkylene) amine component. The
21 ratio of the polyalkylphenoxyalkyl aromatic ester to
22 poly(oxyalkylene) amine will generally range from about
23 0.05:1 to about 5:1, and will preferably be about 2:1 or
24 less.
25
26 The fuel additive composition of the present invention may
27 be formulated as a concentrate using an inert stable
28 oleophilic (i.e., dissolves in gasoline) organic solvent
29 boiling in the range of about 150°F. to 400°F. (about 65°C.
30 to 205°C.). Preferably, an aliphatic or an aromatic
31 hydrocarbon solvent is used, such as benzene, toluene,
32 xylene or higher-boiling aromatics or aromatic thinners.
33 Aliphatic alcohols containing about 3 to 8 carbon atoms,
34 such as isopropanol, isobutylcarbinol, n-butanol and the

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01 like, in combination with hydrocarbon solvents are also
02 suitable for use with the present additives. In the
03 concentrate, the amount of the additive will generally range
04 from about 10 to about 70 weight percent, preferably 10 to
05 50 weight percent, more preferably from 20 to 40 weight
06 percent.

07
08 In gasoline fuels, other fuel additives may be employed with
09 the additive composition of the present invention,
10 including, for example, oxygenates, such as t-butyl methyl
11 ether, antiknock agents, such as methylcyclopentadienyl
12 manganese tricarbonyl, and other dispersants/detergents,
13 such as hydrocarbyl amines, or succinimides. Additionally,
14 antioxidants, metal deactivators, demulsifiers and
15 carburetor or fuel injector detergents may be present.

16
17 In diesel fuels, other well-known additives can be employed,
18 such as pour point depressants, flow improvers, cetane
19 improvers, and the like.

20
21 A fuel-soluble, nonvolatile carrier fluid or oil may also be
22 used with the fuel additive composition of this invention.
23 The carrier fluid is a chemically inert hydrocarbon-soluble
24 liquid vehicle which substantially increases the nonvolatile
25 residue (NVR), or solvent-free liquid fraction of the fuel
26 additive composition while not overwhelmingly contributing
27 to octane requirement increase. The carrier fluid may be a
28 natural or synthetic fluid, such as mineral oil, refined
29 petroleum oils, synthetic polyalkanes and alkenes, including
30 hydrogenated and unhydrogenated polyalphaolefins, and
31 synthetic polyoxyalkylene-derived fluids, such as those
32 described, for example, in U.S. Patent No. 4,191,537 to
33 Lewis, and polyesters, such as those described, for example,
34 in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to

01 Vogel et al., and in European Patent Application
02 Nos. 356,726, published March 7, 1990, and 382,159,
03 published August 16, 1990.

04
05 These carrier fluids are believed to act as a carrier for
06 the fuel additive composition of the present invention and
07 to assist in removing and retarding deposits. The carrier
08 fluid may also exhibit synergistic deposit control
09 properties when used in combination with the fuel additive
10 composition of this invention.

11
12 The carrier fluids are typically employed in amounts ranging
13 from about 25 to about 5000 ppm by weight of the hydrocarbon
14 fuel, preferably from 100 to 3000 ppm of the fuel.
15 Preferably, the ratio of carrier fluid to deposit control
16 additive will range from about 0.2:1 to about 10:1, more
17 preferably from 0.5:1 to 3:1.

18
19 When employed in a fuel concentrate, carrier fluids will
20 generally be present in amounts ranging from about 20 to
21 about 60 weight percent, preferably from 30 to 50 weight
22 percent.

23
24 PREPARATIONS AND EXAMPLES

25
26 A further understanding of the invention can be had in the
27 following nonlimiting Examples. Wherein unless expressly
28 stated to the contrary, all temperatures and temperature
29 ranges refer to the Centigrade system and the term "ambient"
30 or "room temperature" refers to about 20°C. to 25°C. The
31 term "percent" or "%" refers to weight percent and the term
32 "mole" or "moles" refers to gram moles. The term
33 "equivalent" refers to a quantity of reagent equal in moles,
34 to the moles of the preceding or succeeding reactant recited

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01 in that example in terms of finite moles or finite weight or
02 volume. Where given, proton-magnetic resonance spectrum
03 (p.m.r. or n.m.r.) were determined at 300 MHz, signals are
04 assigned as singlets (s), broad singlets (bs), doublets (d),
05 double doublets (dd), triplets (t), double triplets (dt),
06 quartets (q), and multiplets (m), and cps refers to cycles
07 per second.

08

09

Example 1

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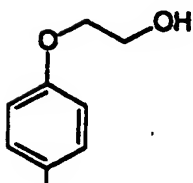
Preparation of Polyisobutyl Phenol

12

13 To a flask equipped with a magnetic stirrer, reflux
14 condenser, thermometer, addition funnel and nitrogen inlet
15 was added 203.2 grams of phenol. The phenol was warmed to
16 40°C. and the heat source was removed. Then,
17 73.5 milliliters of boron trifluoride etherate was added
18 dropwise. 1040 grams of Ultravis 10 Polyisobutene
19 (molecular weight 950, 76% methylvinylidene, available from
20 British Petroleum) was dissolved in 1,863 milliliters of
21 hexane. The polyisobutene was added to the reaction at a
22 rate to maintain the temperature between 22°C. to 27°C. The
23 reaction mixture was stirred for 16 hours at room
24 temperature. Then, 400 milliliters of concentrated ammonium
25 hydroxide was added, followed by 2,000 milliliters of
26 hexane. The reaction mixture was washed with water
27 (3 X 2,000 milliliters), dried over magnesium sulfate,
28 filtered and the solvents removed under vacuum to yield
29 1,056.5 grams of a crude reaction product. The crude
30 reaction product was determined to contain 80% of the
31 desired product by proton NMR and chromatography on silica
32 gel eluting with hexane, followed by hexane: ethylacetate:
33 ethanol (93:5:2).

34

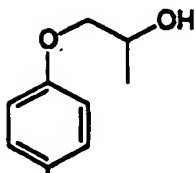
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Example 2Preparation of

PB (molecular weight ~ 950)

1.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (99.7 grams, prepared as in Example 1) were added to a flask equipped with a magnetic stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Ethylene carbonate (8.6 grams) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and one milliliter of isopropanol was added. The reaction was diluted with one liter of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 98.0 grams of the desired product as a yellow oil.

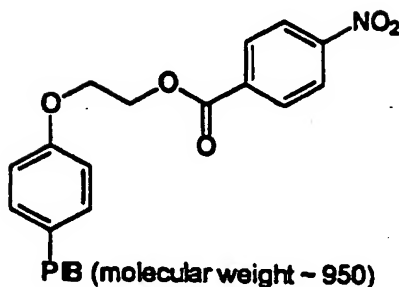
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Example 1Preparation of

PIB (molecular weight ~ 950)

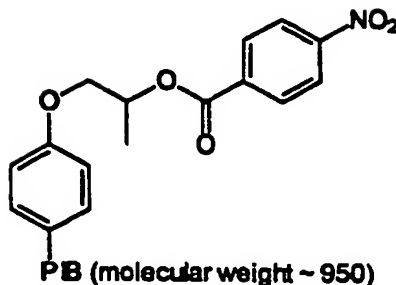
15.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 1301.7 grams of the desired product as a yellow oil.

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Example 4Preparation of

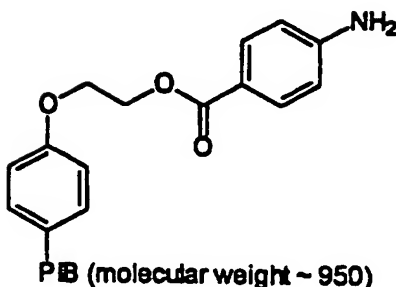
To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 15.0 grams of the alcohol from Example 2, 2.6 grams of 4-nitrobenzoic acid and 0.24 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 15.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (9:1) to afford 14.0 grams of the desired ester as a yellow oil. ¹H NMR (CDCl₃) δ 8.3 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 4.7 (t, 2H), 4.3 (t, 2H), 0.7-1.6 (m, 137H).

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Example 5Preparation of

To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 15.0 grams of the alcohol from Example 3, 2.7 grams of 4-nitrobenzoic acid and 0.23 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 16.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (8:2) to afford 15.2 grams of the desired ester as a brown oil. ¹H NMR (CDCl₃) δ 8.2 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 5.55 (hx, 1H), 4.1 (t, 2H), 0.6-1.8 (m, 140H).

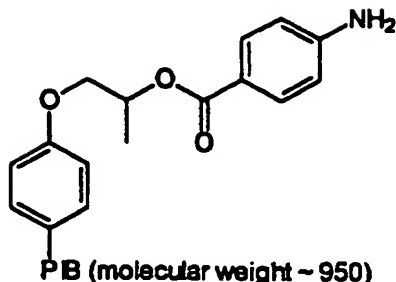
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Example 6Preparation of

A solution of 9.4 grams of the product from Example 4 in 100 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yield 7.7 grams of the desired product as a yellow oil.

^1H NMR (CDCl_3) δ 7.85 (d, 2H), 7.3 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 4.6 (t, 2H), 4.25 (t, 2H), 4.05 (bs, 2H), 0.7-1.6 (m, 137H).

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Example 7Preparation of

A solution of 15.2 grams of the product from Example 5 in 200 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yield 15.0 grams of the desired product as a brown oil.

^1H NMR ($\text{CDCl}_3/\text{D}_2\text{O}$) δ 7.85 (d, 2H), 7.25 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 5.4 (hx, 1H), 3.8-4.2 (m, 4H), 0.6-1.8 (m, 140H).

Example 8

Preparation of Dodecylphenoxy
Poly(oxybutylene)poly(oxypropylene) Amine

A dodecylphenoxypoly(oxybutylene)poly(oxypropylene) amine was prepared by the reductive amination with ammonia of the random copolymer poly(oxyalkylene) alcohol, dodecylphenoxy poly(oxybutylene)poly(oxypropylene) alcohol, wherein the alcohol has an average molecular weight of about 1598. The poly(oxyalkylene) alcohol was prepared from dodecylphenol

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01 using a 75/25 weight/weight ratio of butylene oxide and
02 propylene oxide, in accordance with the procedures described
03 in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as
04 well as in Kirk-Othmer, "Encyclopedia of Chemical
05 Technology", 4th edition, Volume 19, 1996, page 722. The
06 reductive amination of the poly(oxyalkylene) alcohol was
07 carried out using conventional techniques as described in
08 U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

09

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Example 9

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Single-Cylinder Engine Test

13

14 The test compounds were blended in gasoline and their
15 deposit reducing capacity determined in an ASTM/CFR
16 single-cylinder engine test.

17

18 A Waukesha CFR single-cylinder engine was used. Each run
19 was carried out for 15 hours, at the end of which time the
20 intake valve was removed, washed with hexane and weighed.
21 The previously determined weight of the clean valve was
22 subtracted from the weight of the valve at the end of the
23 run. The differences between the two weights is the weight
24 of the deposit. A lesser amount of deposit indicates a
25 superior additive. The operating conditions of the test
26 were as follows: water jacket temperature 200°F; intake
27 manifold vacuum of 12 in. Hg, air-fuel ratio of 12, ignition
28 spark timing of 40 BTC; engine speed is 1800 rpm; the
29 crankcase oil is a commercial 30W oil.

30

31 The amount of carbonaceous deposit in milligrams on the
32 intake valves is reported for each of the test compounds in
33 Table I.

34

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TABLE I**Intake Valve Deposit Weight
(in milligrams)**

Sample¹	Run 1	Run 2	Average
Base Fuel	354.9	333.5	344.2
Example 4	169.0	178.0	173.5
Example 6	13.4	12.2	12.8

¹At 150 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 150 ppma (parts per million actives).

The data in Table I illustrates the significant reduction in intake valve deposits provided by the aromatic ester component of the present invention (Examples 4 and 6) compared to the base fuel.

Example 10Multicylinder Engine Test

The fuel additive composition of the present invention was tested in a laboratory multicylinder engine to evaluate their intake valve and combustion chamber deposit control performance. The test engine was a 2.3 liter, port fuel injected, 4-cylinder single overhead cam engine manufactured by Ford Motor Company. The major engine dimensions are set forth in Table II.

Table II

Engine Dimensions

Bore	9.60 cm
Stroke	7.94 cm
Displacement Volume	2.30 liter
Compression Ratio	9.50:1

The test engine was operated for 60 hours (24 hours a day) on a test cycle developed by the Coordinating Research Council (CRC). The cycle for engine operation during the test is set forth in Table III.

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Table III

Engine Operating Cycle

Stage	Length of Time ¹ (Min:Sec)	Engine Speed [RPM]	Manifold Absolute Pressure [mm Hg]
1	4:00	2000 ± 10	230 ± 10
2	8:00	2800 ± 10	540 ± 10

¹ All stages include a 30 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table IV.

Table IV

Multicylinder Engine Test Results

Sample	Conc. (ppma)	Intake Valve Deposits, mg	Combustion Chamber Deposits, mg
Base Fuel	---	521	945
Aromatic Ester/ Carrier Fluid ¹	50/50	657	1262
Aromatic Ester/ Poly(oxyalkylene) Amine ²	50/50	262	1087

¹ Mixture of 50 ppm of 4-polyisobutylphenoxyethyl para-aminobenzoate prepared as described in Example 6 and 50 ppm of a dodecylphenoxypoly(oxybutylene) alcohol carrier fluid.

² Mixture of 50 ppm of 4-polyisobutylphenoxyethyl para-aminobenzoate and 50 ppm of dodecylphenoxy poly(oxybutylene)poly(oxypropylene) amine prepared as described in Example 8.

The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel at the indicated concentrations.

The data in Table IV demonstrates that the combination of a polyalkylphenoxyalkyl aromatic ester and a poly(oxyalkylene) amine has a synergistic effect and gives significantly better intake valve deposit control than the aromatic ester component with a carrier fluid. Moreover, the data in Table IV further demonstrates that the combination of aromatic ester and poly(oxyalkylene) amine produces fewer combustion chamber deposits than the aromatic ester component with a carrier fluid.

01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) an aromatic ester compound of the formula:

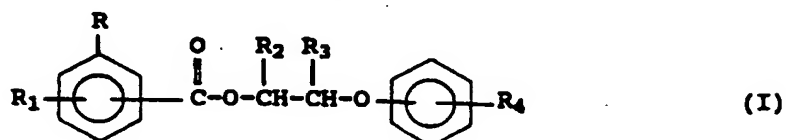
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or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

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R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

20

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22

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

23

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26

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and

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(b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel fuel range.

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- 01 2. The fuel additive composition according to Claim 1,
02 wherein R is nitro, amino or $-\text{CH}_2\text{NH}_2$.
- 03 3. The fuel additive composition according to Claim 2,
04 wherein R is amino, or $-\text{CH}_2\text{NH}_2$.
05
- 06 4. The fuel additive composition according to Claim 3,
07 wherein R is amino.
08
- 09 5. The fuel additive composition according to Claim 1,
10 wherein R_1 is hydrogen, hydroxy, nitro or amino.
- 11 6. The fuel additive composition according to Claim 5,
12 wherein R_1 is hydrogen or hydroxy.
13
- 14 7. The fuel additive composition according to Claim 6,
15 wherein R_1 is hydrogen.
16
- 17 8. The fuel additive composition according to Claim 1,
18 wherein one of R_2 and R_3 is hydrogen or lower alkyl of
19 1 to 4 carbon atoms, and the other is hydrogen.
- 20 9. The fuel additive composition according to Claim 8,
21 wherein one of R_2 and R_3 is hydrogen, methyl or ethyl,
22 and the other is hydrogen.
23
- 24 10. The fuel additive composition according to Claim 9,
25 wherein R_2 is hydrogen, methyl or ethyl, and R_3 is
26 hydrogen.
27
- 28 11. The fuel additive composition according to Claim 1,
29 wherein R_4 is a polyalkyl group having an average
30 molecular weight in the range of about 500 to 3,000.
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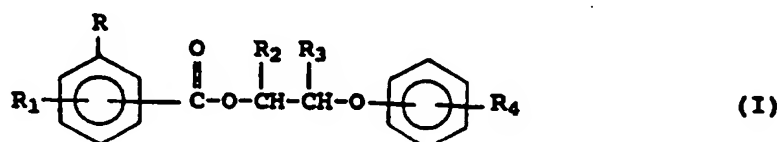
- 01
02
03 12. The fuel additive composition according to Claim 11,
04 wherein R_4 is a polyalkyl group having an average
05 molecular weight in the range of about 700 to 3,000.
06
07 13. The fuel additive composition according to Claim 12,
08 wherein R_4 is a polyalkyl group having an average
09 molecular weight in the range of about 900 to 2,500.
10
11 14. The fuel additive composition according to Claim 1,
12 wherein R_4 is a polyalkyl group derived from
13 polypropylene, polybutene, or a polyalphaolefin
14 oligomer of 1-octene or 1-decene.
15
16 15. The fuel additive composition according to Claim 14,
17 wherein R_4 is a polyalkyl group derived from
18 polyisobutene.
19
20 16. The fuel additive composition according to Claim 15,
21 wherein the polyisobutene contains at least about 20%
22 of a methylvinylidene isomer.
23
24 17. The fuel additive composition according to Claim 1,
25 wherein R is amino, R_1 , R_2 and R_3 are hydrogen and R_4
26 is a polyalkyl group derived from polyisobutene.
27
28 18. The fuel additive composition according to Claim 1,
29 wherein said poly(oxyalkylene) amine has a molecular
30 weight in the range of about 500 to about 10,000.
31
32 19. The fuel additive composition according to Claim 1,
33 wherein said poly(oxyalkylene) amine contains at least
34 about 5 oxyalkylene units.

- 01 20. The fuel additive composition according to Claim 1,
02 wherein said poly(oxyalkylene) amine is a hydrocarbyl
03 poly(oxyalkylene) polyamine.
- 04 21. The fuel additive composition according to Claim 1,
05 wherein said poly(oxyalkylene) amine is a hydrocarbyl
06 poly(oxyalkylene) aminocarbamate.
07
- 08 22. The fuel additive composition according to Claim 21,
09 wherein the hydrocarbyl group of said hydrocarbyl
10 poly(oxyalkylene) aminocarbamate contains from 1 to
11 about 30 carbon atoms.
12
- 13 23. The fuel additive composition according to Claim 22,
14 wherein said hydrocarbyl group of said hydrocarbyl
15 poly(oxyalkylene) aminocarbamate is an alkylphenyl
16 group.
- 17 24. The fuel additive composition according to Claim 23,
18 wherein the alkyl moiety of said alkylphenyl group is
19 tetrapropenyl.
20
- 21 25. The fuel additive composition according to Claim 21,
22 wherein the amine moiety of said hydrocarbyl
23 poly(oxyalkylene) aminocarbamate is derived from a
24 polyamine having from 2 to 12 amine nitrogen atoms and
25 from 2 to 40 carbon atoms.
26
- 27 26. The fuel additive composition according to Claim 25,
28 wherein said polyamine is a polyalkylene polyamine
29 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon
30 atoms.
- 31 27. The fuel additive composition according to Claim 26,
32 wherein said polyalkylene polyamine is selected from
33 the group consisting of ethylenediamine,
34

- 01 propylenediamine, diethylenetriamine and
02 dipropylenetriamine.
- 03 28. The fuel additive composition according to Claim 21,
04 wherein the poly(oxyalkylene) moiety of said
05 hydrocarbyl poly(oxyalkylene) aminocarbamate is derived
06 from C₂ to C₅ oxyalkylene units.
07
- 08 29. The fuel additive composition according to Claim 21,
09 wherein said hydrocarbyl poly(oxyalkylene)
10 aminocarbamate is an alkylphenyl poly(oxybutylene)
11 aminocarbamate, wherein the amine moiety is derived
12 from ethylenediamine or diethylenetriamine.
13
- 14 30. The fuel additive composition according to Claim 1,
15 wherein said poly(oxyalkylene) amine is a hydrocarbyl
16 poly(oxyalkylene) monoamine.
- 17 31. The fuel additive composition according to Claim 30,
18 wherein said hydrocarbyl poly(oxyalkylene) monoamine is
19 an alkylphenyl poly(oxyalkylene) monoamine, wherein the
20 poly(oxyalkylene) moiety contains oxypropylene units or
21 oxybutylene units or mixtures thereof.
22
- 23 32. The fuel additive composition according to Claim 31,
24 wherein the alkylphenyl group is tetrapropenylphenyl.
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33. A fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective deposit-controlling amount of a fuel additive composition comprising:

(a) an aromatic ester compound of the formula:



or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(\text{CH}_2)_x - \text{NR}_5\text{R}_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

R_1 is hydrogen, hydroxy, nitro or $-\text{NR}_7\text{R}_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and

(b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene)

- 01 amine soluble in hydrocarbons boiling in the
02 gasoline or diesel fuel range.
- 03 34. The fuel composition according to Claim 33, wherein R
04 is nitro, amino or $-\text{CH}_2\text{NH}_2$.
05
- 06 35. The fuel composition according to Claim 34, wherein R
07 is amino, or $-\text{CH}_2\text{NH}_2$.
08
- 09 36. The fuel composition according to Claim 35, wherein R
10 is amino.
- 11 37. The fuel composition according to Claim 33, wherein R_1
12 is hydrogen, hydroxy, nitro or amino.
13
- 14 38. The fuel composition according to Claim 37, wherein R_1
15 is hydrogen or hydroxy.
16
- 17 39. The fuel composition according to Claim 38, wherein R_1
18 is hydrogen.
- 19 40. The fuel composition according to Claim 33, wherein one
20 of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4
21 carbon atoms, and the other is hydrogen.
22
- 23 41. The fuel composition according to Claim 40, wherein one
24 of R_2 and R_3 is hydrogen, methyl or ethyl, and the
25 other is hydrogen.
26
- 27 42. The fuel composition according to Claim 41, wherein R_2
28 is hydrogen, methyl or ethyl, and R_3 is hydrogen.
- 29 43. The fuel composition according to Claim 33, wherein R_4
30 is a polyalkyl group having an average molecular weight
31 in the range of about 500 to 3,000.
32
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- 01
02
03 44. The fuel composition according to Claim 43, wherein R₄
04 is a polyalkyl group having an average molecular weight
05 in the range of about 700 to 3,000.
06 45. The fuel composition according to Claim 44, wherein R₄
07 is a polyalkyl group having an average molecular weight
08 in the range of about 900 to 2,500.
09
10 46. The fuel composition according to Claim 33, wherein R₄
11 is a polyalkyl group derived from polypropylene,
12 polybutene, or a polyalphaolefin oligomer of 1-octene
13 or 1-decene.
14
15 47. The fuel composition according to Claim 46, wherein R₄
16 is a polyalkyl group derived from polyisobutene.
17
18 48. The fuel composition according to Claim 47, wherein the
19 polyisobutene contains at least about 20% of a
20 methylvinylidene isomer.
21
22 49. The fuel composition according to Claim 33, wherein R
23 is amino, R₁, R₂ and R₃ are hydrogen and R₄ is a
24 polyalkyl group derived from polyisobutene.
25
26 50. The fuel composition according to Claim 33, wherein the
27 composition contains from about 25 to about 2,000 parts
28 per million by weight of said aromatic ester compound
29 and about 25 to about 2,000 parts per million of said
30 poly(oxyalkylene) amine.
31
32 51. The fuel composition according to Claim 33, where the
33 composition further contains from about 25 to about
34 5,000 parts per million by weight of a fuel-soluble,
nonvolatile carrier fluid.

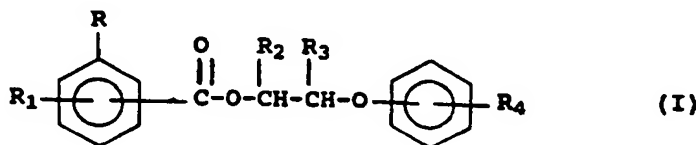
- 01 52. The fuel composition according to Claim 33, wherein
02 said poly(oxyalkylene) amine is a hydrocarbyl
03 poly(oxyalkylene) aminocarbamate.
- 04 53. The fuel composition according to Claim 52, wherein the
05 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)
06 aminocarbamate contains from 1 to about 30 carbon
07 atoms; and wherein the amine moiety of said hydrocarbyl
08 poly(oxyalkylene) aminocarbamate is derived from a
09 polyamine having from 2 to 12 amine nitrogen atoms and
10 from 2 to 40 carbon atoms.
11
- 12 54. The fuel composition according to Claim 53, wherein
13 said hydrocarbyl group of said hydrocarbyl
14 poly(oxyalkylene) aminocarbamate is an alkylphenyl
15 group; and wherein said polyalkylene polyamine is
16 selected from the group consisting of ethylenediamine,
17 propylenediamine, diethylenetriamine and
18 dipropylenetriamine.
19
- 20 55. The fuel composition according to Claim 54, wherein the
21 alkyl moiety of said alkylphenyl group is
22 tetrapropenyl.
- 23 56. The fuel composition according to Claim 52, wherein
24 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an
25 alkylphenyl poly(oxybutylene) aminocarbamate, wherein
26 the amine moiety is derived from ethylenediamine or
27 diethylenetriamine.
28
- 29 57. The fuel composition according to Claim 33, wherein
30 said poly(oxyalkylene) amine is a hydrocarbyl
31 poly(oxyalkylene) monoamine.
32
- 33 58. The fuel composition according to Claim 57, wherein
34 said hydrocarbyl poly(oxyalkylene) monoamine is an

01 alkylphenyl poly(oxyalkylene) monoamine, wherein the
 02 poly(oxyalkylene) moiety contains oxypropylene units or
 03 oxybutylene units or mixtures thereof.

04 59. The fuel composition according to Claim 58, wherein the
 05 alkylphenyl group is tetrapropenylphenyl.
 06

07 60. A fuel concentrate comprising an inert stable
 08 oleophilic organic solvent boiling in the range of from
 09 about 150°F. to 400°F. and from about 10 to about
 10 70 weight percent of a fuel additive composition
 11 comprising:
 12

13 (a) an aromatic ester compound of the formula:
 14
 15
 16



21 or a fuel soluble salt thereof, wherein R is
 22 hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6
 23 are independently hydrogen or lower alkyl having 1
 24 to 6 carbon atoms and x is 0 or 1;
 25

26 R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein
 27 R_7 and R_8 are independently hydrogen or lower
 28 alkyl having 1 to 6 carbon atoms;
 29

30 R_2 and R_3 are independently hydrogen or lower
 31 alkyl having 1 to 6 carbon atoms; and
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-60-

- 01 R₄ is a polyalkyl group having an average
02 molecular weight in the range of about 450 to
03 5,000; and
- 04 (b) a poly (oxyalkylene) amine having at least one
05 basic nitrogen atom and a sufficient number of
06 oxyalkylene units to render the poly(oxyalkylene) amine
07 soluble in hydrocarbons boiling in the gasoline or
08 diesel fuel range.
09
- 10 61. The fuel concentrate according to Claim 60, wherein R
11 is nitro, amino or -CH₂NH₂.
12
- 13 62. The fuel concentrate according to Claim 61, wherein R
14 is amino, or -CH₂NH₂.
15
- 16 63. The fuel concentrate according to Claim 62, wherein R
17 is amino.
18
- 19 64. The fuel concentrate according to Claim 60, wherein R₁
20 is hydrogen, hydroxy, nitro or amino.
21
- 22 65. The fuel concentrate according to Claim 64, wherein R₁
23 is hydrogen or hydroxy.
24
- 25 66. The fuel concentrate according to Claim 65, wherein R₁
26 is hydrogen.
27
- 28 67. The fuel concentrate according to Claim 60, wherein one
29 of R₂ and R₃ is hydrogen or lower alkyl of 1 to
30 4 carbon atoms, and the other is hydrogen.
31
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- 01 68. The fuel concentrate according to Claim 67, wherein one
02 of R₂ and R₃ is hydrogen, methyl or ethyl, and the
03 other is hydrogen.
04
- 05 69. The fuel concentrate according to Claim 68, wherein R₂
06 is hydrogen, methyl or ethyl, and R₃ is hydrogen.
07
- 08 70. The fuel concentrate according to Claim 60, wherein R₄
09 is a polyalkyl group having an average molecular weight
10 in the range of about 500 to 3,000.
11
- 12 71. The fuel concentrate according to Claim 70, wherein R₄
13 is a polyalkyl group having an average molecular weight
14 in the range of about 700 to 3,000.
15
- 16 72. The fuel concentrate according to Claim 71, wherein R₄
17 is a polyalkyl group having an average molecular weight
18 in the range of about 900 to 2,500.
19
- 20 73. The fuel concentrate according to Claim 60, wherein R₄
21 is a polyalkyl group derived from polypropylene,
22 polybutene, or a polyalphaolefin oligomer of 1-octene
23 or 1-decene.
24
- 25 74. The fuel concentrate according to Claim 73, wherein R₄
26 is a polyalkyl group derived from polyisobutene.
27
- 28 75. The fuel concentrate according to Claim 74, wherein the
29 polyisobutene contains at least about 20% of a
30 methylvinylidene isomer.
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- 01 76. The fuel concentrate according to Claim 60, wherein R
02 is amino, R₁, R₂ and R₃ are hydrogen and R₄ is a
03 polyalkyl group derived from polyisobutene.
04
- 05 77. The fuel concentrate according to Claim 60, wherein the
06 fuel concentrate further contains from about 20 to
07 about 60 weight percent of a fuel-soluble, nonvolatile
08 carrier fluid.
09
- 10 78. The fuel concentrate according to Claim 60, wherein
11 said poly(oxyalkylene) amine is a hydrocarbyl
12 poly(oxyalkylene) aminocarbamate.
13
- 14 79. The fuel concentrate according to Claim 78, wherein the
15 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)
16 aminocarbamate contains from 1 to about 30 carbon
17 atoms; and wherein the amine moiety of said hydrocarbyl
18 poly(oxyalkylene) aminocarbamate is derived from a
19 polyamine having from 2 to 12 amine nitrogen atoms and
20 from 2 to 40 carbon atoms.
- 21 80. The fuel concentrate according to Claim 79, wherein
22 said hydrocarbyl group of said hydrocarbyl
23 poly(oxyalkylene) aminocarbamate is an alkylphenyl
24 group; and wherein said polyalkylene polyamine is
25 selected from the group consisting of ethylenediamine,
26 propylenediamine, diethylenetriamine and
27 dipropylenetriamine.
28
- 29 81. The fuel concentrate according to Claim 80, wherein the
30 alkyl moiety of said alkylphenyl group is
31 tetrapropenyl.
32
- 33 82. The fuel concentrate according to Claim 78, wherein
34 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an

- 01 alkylphenyl poly(oxybutylene) aminocarbamate, wherein
02 the amine moiety is derived from ethylenediamine or
03 diethylenetriamine.
- 04 83. The fuel concentrate according to Claim 60, wherein
05 said poly(oxyalkylene) amine is a hydrocarbyl
06 poly(oxyalkylene) monoamine.
07
- 08 84. The fuel concentrate according to Claim 83, wherein
09 said hydrocarbyl poly(oxyalkylene) monoamine is an
10 alkylphenyl poly(oxyalkylene) monoamine, wherein the
11 poly(oxyalkylene) moiety contains oxypropylene units or
12 oxybutylene units or mixtures thereof.
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- 14 85. The fuel concentrate according to Claim 84, wherein the
15 alkylphenyl group is tetrapropenylphenyl.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07941**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C10L 1/18, 1/22

US CL : 44/399, 400; 560/19, 20, 37, 61, 103

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/399, 400; 560/19, 20, 37, 61, 103

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,515,981 A (OTANI ET AL) 07 May 1985 (07-05-85)	1-85
A	US 5,103,039 A (REARDAN ET AL) 07 April 1992 (07-04-92)	1-85
A	US 5,196,565 A (ROSS) 23 May 1993 (23-05-93)	1-85
A	US 5,366,519 A (CHERPECK) 22 November 1994 (22-11-94)	1-85
A,P	US 5,516,342 A (CHERPECK) 14 May 1996 (14-05-96)	1-85
A,P	US 5,540,743 A (CHERPECK) 30 July 1996 (30-07-96)	1-85

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

Special categories of cited documents:	
A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O document referring to an oral disclosure, use, exhibition or other means	*A* document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

07 JULY 1997

Date of mailing of the international search report

24 JUL 1997

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